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(54) Electrochemical cell incorporating an external hydrogen removing agent

(57) A battery having a hydrogen removing agent disposed on the battery external from the active cell volume of its container for removing hydrogen produced by the electrochemically active materials. The hydrogen removing agent is disposed on a surface of the seal member which is disposed within an open top end of the container, according to one embodiment. According to other embodiments, the hydrogen removing agent is disposed on an inner surface of an outer cover, or disposed on a label on the outside walls of the container. A multi-cell battery is also provided having the hydrogen removing agent disposed on the interior walls thereof.

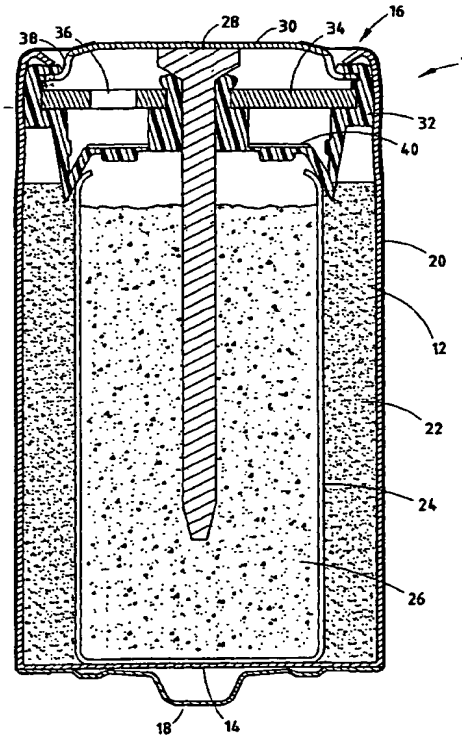

FIG. 1

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Description

[0001] This invention generally relates to batteries and, more particularly, to removing hydrogen accumulation in batteries, and is particularly useful for batteries used in sealed compartments such as in a packaged camera, a sealed flashlight, or other sealed device.

[0002] Conventional alkaline electrochemical cells generally include a steel cylindrical can having a positive electrode, referred to as the cathode, which comprises manganese dioxide as the active material and is generally formed against the interior surface of the steel can. The electrochemical cell also includes a negative electrode, referred to as the anode, which comprises zinc powder and is generally centrally disposed in the can. A separator is located between the anode and the cathode, and an alkaline electrolyte solution simultaneously contacts the anode, cathode, and separator. A conductive current collector is commonly inserted into the anode active material and a seal assembly, which includes a seal member, provides closure to the open end of the cell's steel can to seal the active electrochemical materials in a sealed volume.

[0003] Standard alkaline cells are commercially available for providing an open circuit voltage of about 1.5 volts. When a higher voltage is required, it is common practice to combine multiple cells to form a battery having the required voltage. In doing so, a plurality of cells is commonly housed in a container and electrically connected in series. Additionally, external terminals are attached to the outside of the container for making an electrical connection with the cells.

[0004] It is generally known that small amounts of hydrogen are produced inside an alkaline cell due to corrosion of the anode such as a zinc anode. As is commonly experienced with electrochemical cells, the very small hydrogen gas molecules are capable of being released from the active cell volume of the container by permeating the seal. Typically, a portion of the hydrogen accumulates inside the sealed volume of the battery, while some of the hydrogen permeates through and around the seal, particularly between the current collector and seal, and therefore escapes from the cell's sealed volume. Ventable seals are often used which open and release hydrogen when excessive pressure builds up in the sealed volume.

[0005] Excessive accumulation of hydrogen can present potentially unacceptable conditions, particularly in sealed compartments. For example, hydrogen may become concentrated in the sealed battery compartment of a flashlight or other electrically-operated device, and can potentially lead to problems in operating the device. As another example, a concentration of hydrogen in a disposable camera that is preloaded with photographic film and commercially made available in a sealed airtight package may adversely reduce silver in the film and fog the film, thereby degrading the cameras photographic film.

[0006] Hydrogen getters and recombination catalysts have been available to remove hydrogen. For example, it has been known that hydrogen absorbing materials, such as hydrogen getters and recombination catalysts, can be used to counteract hydrogen accumulation, by disposing the hydrogen removing material in the sealed battery compartment of a battery-operated device such as a flashlight. However, only certain selected electrically-operated devices are made available with a hydrogen removing material. In addition, damage or breakdown of the hydrogen removing agent over time may reduce its effectiveness in the device.

[0007] It is also known to incorporate hydrogen absorbing or removing materials into batteries within the sealed volume of the cell that contains the electrochemically active materials. However, exposure of the hydrogen removing agent to these active materials can lead to deterioration or breakdown of the hydrogen removing agent, and thus reduce its effectiveness.

[0008] Accordingly, it would be desirable to reduce the hydrogen accumulation that may occur present in or around a battery, without the disadvantages until now associated with the use of hydrogen removing agents in batteries or in battery-operated devices. In addition, it would be desirable to be able to reduce an accumulation of hydrogen gas from a battery for use in sealed battery-operated devices such as flashlights, cameras, and especially in such devices preloaded with batteries in a sealed airtight package such as a disposable camera.

[0009] We have now found that this can be achieved by incorporating a hydrogen removing agent in a battery such that the agent is disposed external from the sealed volume of the cell containing the electrochemically active materials.

[0010] Accordingly, in a first aspect, the present invention provides an electrochemical cell or battery comprising electrochemically active materials contained in an active cell volume, and a hydrogen removing agent disposed external from the active cell volume.

[0011] In a second aspect, the present invention provides a packaged battery-operated device pre-packaged with such a cell or battery, for example a disposable camera.

[0012] According to the present invention, a hydrogen removing agent is disposed on the electrochemical cell external to the active cell volume of the can. The hydrogen removing agent removes at least some, and preferably a substantial amount, of the hydrogen accumulation so that excessive hydrogen accumulation can be prevented. This hydrogen removal is especially advantageous when the electrochemical cell is employed in a sealed enclosure such as a flashlight or a camera, as well as other applications.

[0013] The hydrogen removing agent may include any of a number of available agents that effectively remove hydrogen. For example, the hydrogen removing agent may include a hydrogen recombination catalyst or a

hydrogen getter, both of which are known to remove hydrogen. One example of a known hydrogen getter is disclosed in US-A-5,837,158. Hydrogen getters, such as those disclosed in US-A-5,837,158 above, remove hydrogen accumulation by providing a controlled reaction between an organic reactant and hydrogen. An example of a hydrogen recombination catalyst for use as the hydrogen removing agent is one which causes hydrogen and oxygen to combine and produce water. Another example of a suitable hydrogen recombination catalyst is disclosed in US-A-3,893,870. It will be appreciated that other known hydrogen removing agents may be employed, according to the present invention.

[0014] The hydrogen removing agent may be applied to the battery by any of a number of known application techniques including, but not limited to, spraying, painting, printing, or other application techniques. The hydrogen removing agent could for example be applied directly to the desired battery location such as the surface of the seal, or could be applied to a carrier surface, such as a tape material, which in turn can be adhered or otherwise applied to the surface of the seal. It will be appreciated that the hydrogen removing agent may be provided in various shapes, sizes, and locations in or on the battery.

[0015] To prevent excessive pressure build-up in the sealed volume of the container, a pressure release vent may be provided in the seal to open at a predetermined internal pressure to vent internal pressure, including hydrogen, from within the sealed volume of the can.

[0016] Preferably, the electrochemically active material comprises an anode containing zinc, a cathode containing manganese dioxide, and an alkaline electrolyte.

[0017] A current collector is preferably disposed in contact with the cover and extends into the active cell volume of the container, the seal member having an opening extending therethrough to receive the current collector.

[0018] In one example, a battery comprises:

a container having walls defining a volume and including an active cell volume for housing active cell materials;
electrochemically active materials contained in the active cell volume of the container; and
a hydrogen removing agent disposed on the battery external from the active cell volume of the container for removing hydrogen produced by the electrochemically active materials.

[0019] In accordance with a first embodiment, the battey comprises:

a can defining an electrochemical cell and having a closed bottom end and an open top end and side walls extending between the bottom end and top end; and
a seal member disposed within the open top end of the can to close the can and define the active cell volume of the container as the volume between the bottom end and the seal member, and the hydrogen removing agent is disposed on a surface of the seal member external to the active cell volume, preferably on a top surface of the seal member.

[0020] In an example in accordance with the first embodiment, an electrochemical cell comprises:

a container having a closed bottom end and an open top end;
electrochemically active materials disposed in the container, the electrochemically active materials including a positive electrode and a negative electrode;
a seal member disposed in the open end of the container for containing the electrochemically active materials in an active cell volume of the container; and
a hydrogen removing agent disposed on a surface of the seal member external from the active cell volume for removing hydrogen released from the active cell volume of the container.

[0021] In accordance with a second embodiment, the battery comprises:

a can defining an electrochemical cell and having a closed bottom end and an open top end;
an inner seal member disposed in the open top end of the can to seal the electrochemical materials in the can and define the active cell volume;
an outer cover assembled to the open top end of the can, the outer cover and inner seal member defining a container volume therebetween which is external to the active cell volume, and
a hydrogen removing agent disposed in the container volume, preferably on an inner surface of the outer cover.

[0022] In an example in accordance with the second embodiment, an electrochemical cell comprises:

a container having a closed bottom end and an open top end;
electrochemically active materials disposed in the container, the electrochemically active materials including a positive electrode and a negative electrode;
a seal member disposed in the open end of the container for containing the electrochemically active materials in an active cell volume of the container;
a cover assembled to the open end of the container and enclosing the seal member, the cover and seal member defining a container volume external to the active cell volume; and
a hydrogen removing agent disposed in the con-

tainer volume for removing hydrogen released from the active cell volume of the container.

[0023] In an alternative example in accordance with the second embodiment, an electrochemical cell comprises:

a container having a closed bottom end and an open top end;
electrochemically active materials disposed in the can, the electrochemically active materials including a positive electrode and a negative electrode;
an inner seal member disposed in the open end of the container for containing the electrochemically active materials in an active cell volume of the container;
an outer cover assembled to the open top end of the container to close the container; and
a hydrogen removing agent disposed on an interior surface of the outer cover for removing hydrogen released from the active cell volume of the container.

[0024] In accordance with a third embodiment, the battery comprises:

a label formed on an outside wall of the container; and
a hydrogen removing agent disposed on the label.

[0025] In an example in accordance with the third embodiment, an electrochemical cell comprises:

a container having a bottom end, a top end, and side walls extending therebetween;
electrochemically active materials contained in an active cell volume of the container;
a label disposed on an outside surface of the side walls of the container, and
a hydrogen removing agent disposed on the label for removing hydrogen released from the active cell volume of the container.

[0026] In accordance with a fourth embodiment, a battery container houses multiple electrochemical cells, and the hydrogen removing agent is disposed on a surface of the container.

[0027] In an example in accordance with the fourth embodiment, a multi-cell battery comprises:

a container having a bottom side, a top side, and side walls, the container further having one or more battery terminals;
a plurality of electrochemical cells housed in the container, each of the cells containing electrochemically active materials in an active cell volume for providing electrical energy; and
a hydrogen removing agent disposed on the container and external from the active cell volume of the electrochemical cells for removing hydrogen emitted from the electrochemical cells.

[0028] A preferred method of assembling a battery in accordance with the present invention comprises the steps of:

dispensing electrochemically active materials in a container having an open top end and a closed bottom end;
disposing an inner seal member in the open top end of the container to contain the electrochemically active materials in an active cell volume of the container, assembling an outer cover to the open end of the container to close the open end of the container; and
applying a hydrogen removing agent to the battery external from the active cell volume of the container.

[0029] Preferably, the step of applying the hydrogen removing agent comprises applying the hydrogen removing agent to a top surface of the inner seal member, or to a bottom surface of the outer cover, or elsewhere in a container volume defined as the volume between the inner seal member and the outer cover. Alternatively, the step of applying the hydrogen removing agent comprises applying the hydrogen removing agent to a label on the ouside of the container. In another alternative, the method further comprises assembling multiple electrochemical cells in a common housing to form a multi-cell battery, and the step of applying the hydrogen removing agent comprises applying the hydrogen removing agent to the common housing.

[0030] Thus, according to the present invention a hydrogen removing agent is disposed on an electrochemical cell or battery external to the sealed volume containing the electrochemically active materials of the cell, to reduce the amount of hydrogen emitted from the cell into the surrounding atmosphere. The electrochemical cell can be employed in an electrically-operated device such as a flashlight or a camera, which often employ a sealed battery compartment. By providing the hydrogen removing agent on the battery, the amount of hydrogen present in the electrically-operated device can be reduced without having to incorporate a hydrogen removing agent directly into the electrically-operated device.

[0031] The present invention may be further understood by reference to the following examples, their description, and the drawings in which:

Figure 1 is a longitudinal cross-sectional view of an electrochemical cell having a hydrogen removing agent disposed on the top surface of an annular seal member according to a first embodiment of the

present invention;

Figure 2 is an exploded perspective view of the annular seal member containing the hydrogen removing agent as shown in Figure 1;

Figure 3 is a partial longitudinal cross-sectional view of an electrochemical cell having the hydrogen removing agent disposed on a bottom surface of the outer negative cover according to a second embodiment;

Figure 4 is a partial longitudinal cross-sectional view of a electrochemical cell having the hydrogen removing agent disposed on an outer can label according to a third embodiment;

Figure 5 is a partial cutaway view of a multi-cell battery having a hydrogen removing agent disposed on an inside surface of the battery housing according to a fourth embodiment; and

Figure 6 is a comparative graph illustrating the hydrogen volume that is collected from the electrochemical cell shown in Figure 3 stored in a sealed container as compared to the hydrogen volume from an electrochemical cell that does not include the hydrogen removing agent.

[0032] Referring to Figure 1, a cylindrical alkaline electrochemical cell 10 is shown. Alkaline cell 10 includes a cylindrical steel can 12 having a closed bottom end 14 and all open top end 16. The closed bottom end of can 12 further includes a positive cover welded or otherwise attached thereto and formed of plated steel with a protruding nub 18 at its centre region which forms the positive contact terminal of cell 10. Assembled to the open end 16 of the steel can 12 is a cover and seal assembly which forms the negative contact terminal of cell 10. A metalised, plastic film label 20 is formed about the exterior surface of steel can 12, except for the ends of steel can 12. Film label 20 is formed over the peripheral edge of the positive cover.

[0033] A cathode 22, preferably formed of a mixture of manganese dioxide, graphite, forty-five percent potassium hydroxide solution, and additives is formed about the interior surface- of steel can 12. A separator 24, which is preferably formed of a non-woven fabric that prevents migration of any solid particles in the cell, is disposed about the interior surface of cathode 22. An anode 26, preferably formed of zinc powder, a gelling agent, and additives, is disposed with an electrolyte inside the separator 24 and is in contact with a current collector 28, which may include a brass nail. Accordingly, the cathode 22 is configured as the cell's positive electrode, and the anode 26 is configured as the cell's negative electrode.

[0034] The current collector 28 contacts an outer negative cover 30 which forms the negative contact terminal of cell 10. An annular nylon seal 32 is disposed in the open end 16 of the steel can 12 to prevent leakage of the active cell ingredients contained in steel can 12. Nylon seal 32 contacts a metal washer 34 which forms a inner cell cover, and is preferably formed of steel. The outer negative cover 30 is preferably formed of plated steel, and may be held in contact with curtent collector 28 via pressure contact or a weld. It should be appreciated that the outer negative cover 30 is electrically insulated from the steel can 12 by way of nylon seal 32. In addition, the inner cover 34 includes one or more vent openings 36. The outer negative cover 30 also includes one or more openings 38 to vent pressure build-up from within the cell 10 to the outside atmosphere. Together, the current collector 28, seal 32 and inner cover 34 form the cover and seal assembly that is inserted into the open end 16 of can 12 to seal the active ingredients therein.

[0035] According to a first embodiment as shown in Figures 1 and 2, the hydrogen removing agent 40 is disposed on a top surface 42 of the annular seal 32. The hydrogen removing agent 40 is shown in the form of a thin circular disk having a opening through which an axial boss 44 of seal 32 extends. The hydrogen removing agent 40 is applied to the surface 42 of the annular seal 32 external to the cell's electrochemically active components, yet it is within the overall volume of the battery such that it is exposed to hydrogen which leaks from the electrochemically active volume of the cell to the outside environment.

[0036] Referring to Figure 3, the hydrogen removing agent 40 is shown disposed on the inside surface of the outer negative cover 30 according to a second embodiment of the present invention. The hydrogen removing agent 40 may be applied to the bottom surface of outer negative cover 30 in various shapes, sizes, and locations, and in a manner similar to that disposed on the seal 32 according to the first embodiment. It should be appreciated that the hydrogen removing agent 40 of the first and second embodiments, is advantageously located external from the internal volume containing the electrochemically active materials of cell 10, yet within the entire volume of the cell 10, and more particularly in the volume defined between the seal 32 and outer negative cover 30. It should also be appreciated that the hydrogen removing agent 40 may he located in other locations on the cell 10 external from the active cell volume containing the electrochemically active materials. For example, the hydrogen removing agent 40 could likewise be disposed on the current collector 28 at a location between seal 32 and outer negative cover 30. As another example, the hydrogen removing agent 40 could be disposed on the inner cover 34, Accordingly, the hydrogen removing agent 40 is disposed preferably in a location where it will be exposed to hydrogen released from the active materials of the electrochemical cell 10.

[0037] Referring to Figure 4, an electrochemical cell 10 is shown having the hydrogen removing agent 40 disposed outside of the steel can 12 on the outer surface of label 20. In this embodiment, the hydrogen removing agent 40 may be applied in the shape of a

ring, and is made available for exposure to hydrogen that is released from the electrochemical cell 10 to the outside atmosphere. It should be appreciated that the hydrogen removing agent 40 may likewise be disposed at other locations on the outside surface of cell 10. For example, the hydrogen removing agent 40 could he disposed on the outer surface of outer negative cover 30. Also, hydrogen removing agent 40 could be disposed on the inner or outer surface of the positive cover. In addition, the hydrogen removing agent 40 could be integrally formed in the label 20.

[0038] Referring to Figure 5, a multi-cell battery 50 is illustrated therein which contains a plurality of electrochemical cells 10. The multi-cell battery 50 may include six electrochemical cells 10 connected in series to form a 9-volt battery as is generally known in the battery art. The multi-cell battery 50 includes a container 52 housing the multiple electrochemical cells 10, and has positive and negative contact terminals 54 and 56 provided on the top end of the container 52. The multi-cell battery 50 has the hydrogen removing agent 40 preferably located on an inside surface, such as the inner side walls of the container 52, to remove hydrogen accumulation emitted from the electrochemical cells 10. While the hydrogen removing agent 40 is shown on the inside surface of the side walls of container 52, it should also be appreciated that the hydrogen removing agent 40 may be located on the top or bottom inside walls, or an outer surface of one or more of the electrochemical cells 10, or may be located on an outside surface of the container 52.

[0039] With particular reference to Figure 6, a graph is shown which illustrates the performance of electrochemical cells having a hydrogen removing agent in the form of a hydrogen recombination catalyst applied to the inside surface of outer negative cover 30 as shown in Figure 3, and compared to similar electrochemical cells without the hydrogen removing agent 40. In particular, cylindrical alkaline AA-sized cells were tested over a two week period at temperatures of 50°C and 71°C. Hydrogen volume measurements were taken by placing the cells at the corresponding temperature in a bag for the two week test period. The total volume of air in the bag was measured. The air was analysed for hydrogen concentration and the volume of air was multiplied by the percentage of hydrogen to arrive at the hydrogen volume measurement. Two cells containing the hydrogen removing agent 40 on the bottom surface of the outer negative cover 30 were tested, and the volume of hydrogen accumulated in each cell was measured. The hydrogen volume measurement for one cell tested at 50°C is identified by reference numeral 64, and the hydrogen volume measurement for the other cell tested at 71°C is shown by reference numeral 66. In contrast, the conventional cells, which did not include the hydrogen removing agent, provided much greater hydrogen volume measurements as identified by reference numeral 60 for the 50°C test, and reference numeral 62 for the 71°C test. As shown, the hydrogen removing agent 40 significantly reduced the volume of hydrogen accumulation in the cell, when contrasted to the conventional cells not containing the hydrogen removing agent. In addition, the graphs shown in Figure 6 illustrate that the amount of hydrogen accumulation tends to be greater when the temperature is increased.

Claims

1. An electrochemical cell or battery, comprising electrochemically active materials contained in an active cell volume, and a hydrogen removing agent disposed external from the active cell volume.

2. A cell/battery according to claim 1, comprising a can containing the electrochemically active materials and closed with a seal member, the internal volume of the closed can defining a sealed active cell volume.

3. A cell/battery according to claim 2 wherein the hydrogen removing agent is disposed on a surface of the seal member external to the sealed active cell volume.

4. A cell/battery according to claim 3 wherein the hydrogen removing agent is disposed on a top surface of the seal member.

5. A cell/battery according to any of claims 2 to 4 wherein a cover is assembled to the can over the seal member, and the hydrogen removing agent is disposed in the volume between the seal member and the cover.

6. A cell/battery according to any of claims 2 to 5 wherein a cover is assembled to the can over the seal member and the hydrogen removing agent is disposed on a surface of the cover.

7. A cell/battery according to any preceding claim, wherein a label is disposed on an outside wall of the can and the hydrogen removing agent is disposed on the label.

8. A cell/battery according to any of claims 2 to 7 wherein the seal member is adapted to vent hydrogen gas from the sealed active cell volume.

9. A cell/battery according to any preceding claim wherein the hydrogen removing agent comprises a hydrogen recombination catalyst, a hydrogen getter, or both.

10. A cell/battery according to any of claims 5 to 9, wherein a current collector is disposed in contact with the cover and extends through the seal mem-

ber into the active cell volume.

11. A multi-cell battery comprising a plurality of cells as defined in any preceding claim, wherein the hydrogen removing agent is disposed external from the active cell volumes of each of the cells.

12. A packaged battery-operated device prepackaged with a battery according to any preceding claim.

13. A device according to claim 12 wherein the device is a disposable camera.

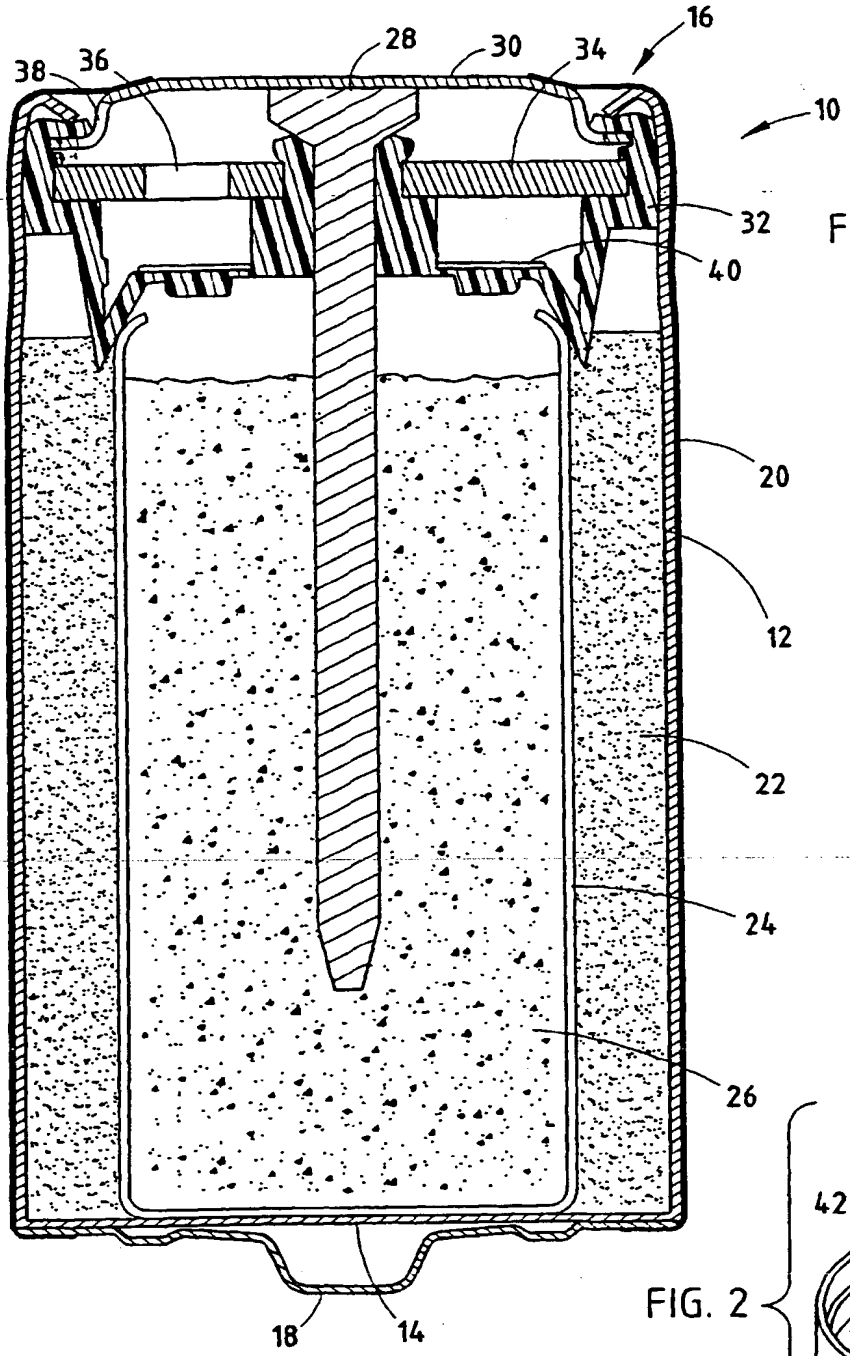

FIG. 1

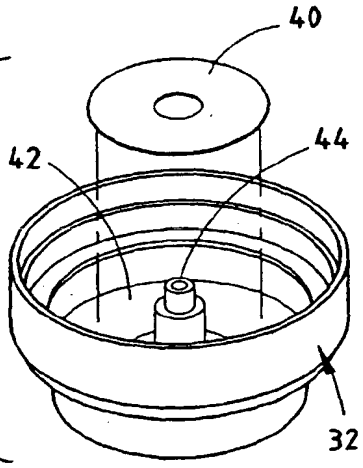

FIG. 2

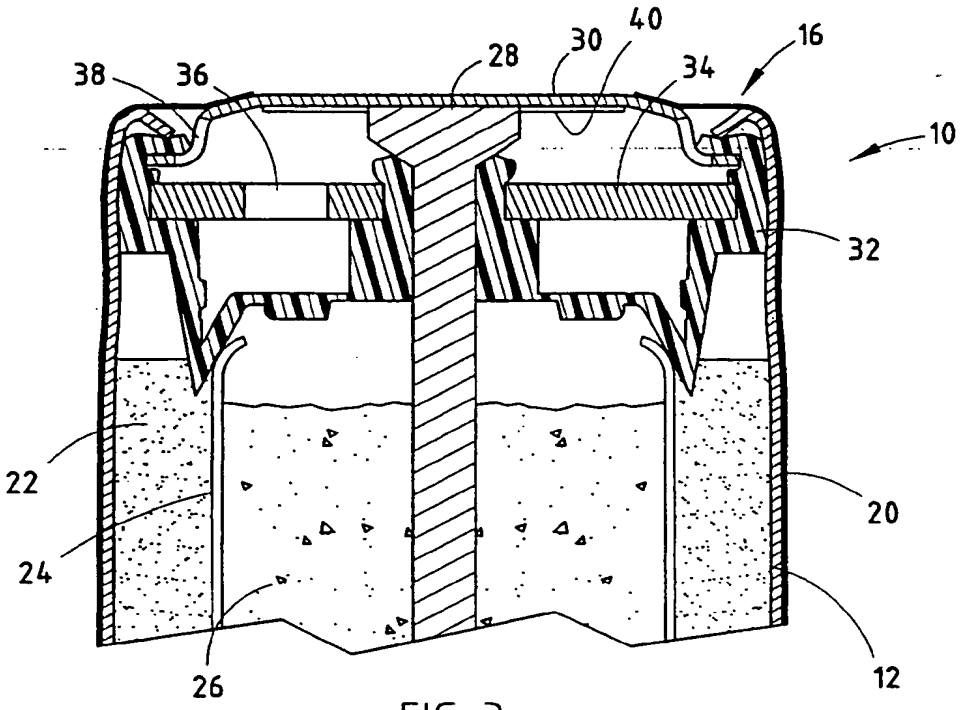

FIG. 3

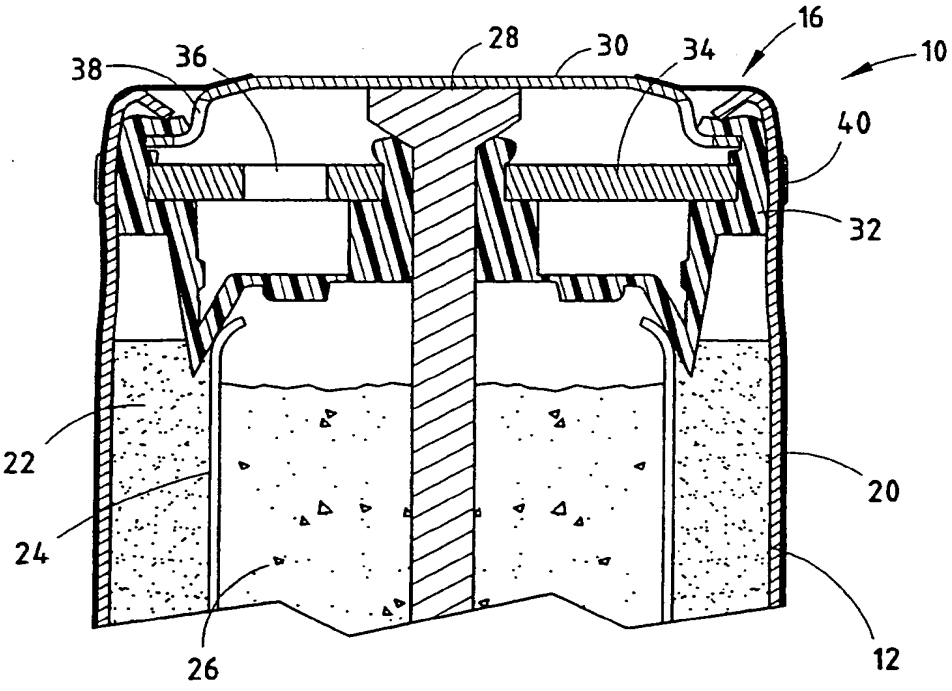

FIG. 4

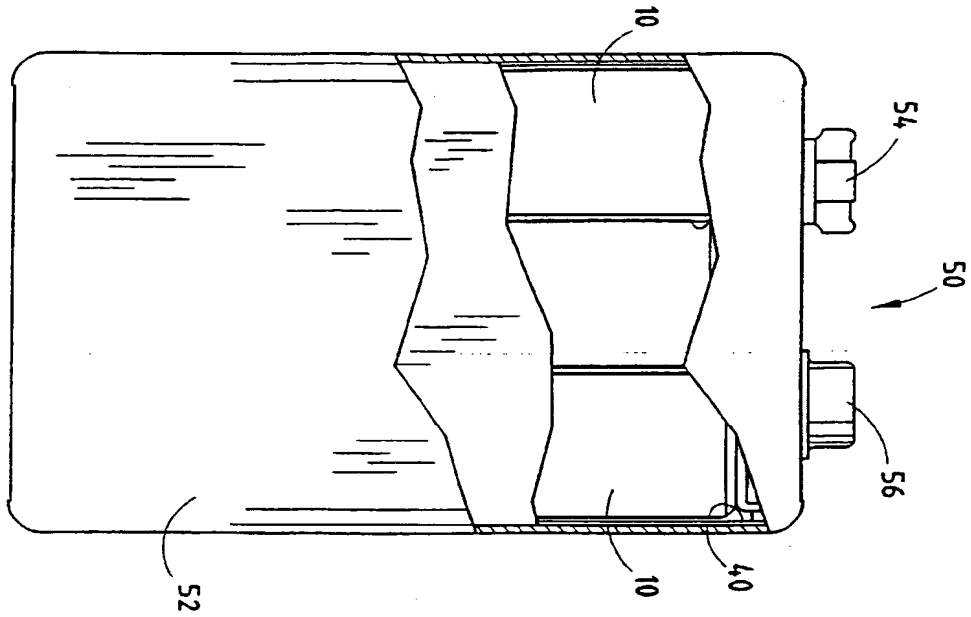

FIG. 5

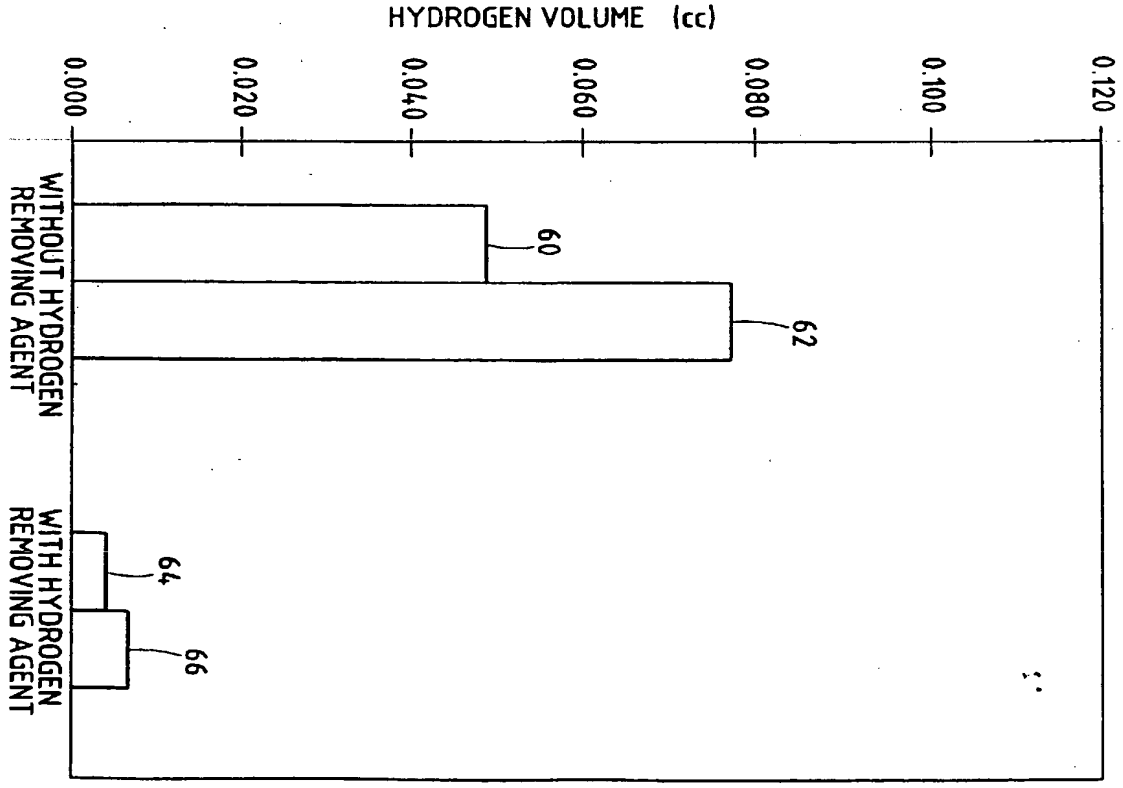

FIG. 6

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EUROPEAN SEARCH REPORT

Application Number
EP 99 30 2667

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	14 July 1999	De Vos, L

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
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D : document cited in the application
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Place of search	Date of completion of the search	Examiner
THE HAGUE	14 July 1999	De Vos, L

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